Study by First-Principles calculation of structure and electronic property of perovskite-type mixed-valence compound $Cs_2Au^IAu^{III}Cl_6$ and its analogues, $Cs_2Ag^IAu^{III}Cl_6$ $Cs_2Cu^IAu^{III}Cl_6$

([1]*Graduate School of Science and Technology, Shinshu University*) ○Keita Soma,[1] Hiroshi Ohki,[1] Atsushi Ishikawa,[1] Akari Takeuch[1]
Keywords: mixed-valence compound

[Introduction] Mixed-valence compound $Cs_2Au^IAu^{III}Cl_6$ is known for showing semiconductor-metal transition by changing crystal structure at high pressure. On the other hand, quantitative correlation study between crystal structure and band gap is not studied yet. In this report, these correlations were estimated by first-principles calculation software Wien2k. And we synthesized analogues of $Cs_2Au^IAu^{III}Cl_6$ and compared band gap through diffuse reflectance measurement.

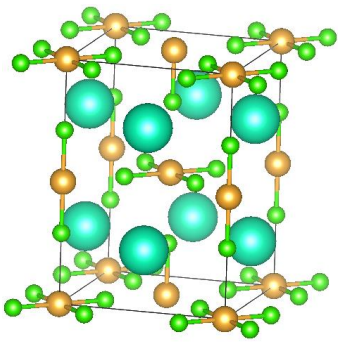

Fig.1 Crystal structure of $Cs_2Au^IAu^{III}Cl_6$

[Experiments] Crystal structure of $Cs_2Au^IAu^{III}Cl_6$ is shown in Fig.1.In the calculation, change of crystal structure by a pressure can be divided into four parts: (1) contraction of *a*,*b*-axes, (2) contraction of *c*-axis, (3) moving 8*h* site Cl atoms to Au-Au mid-position, (4) moving 4*e* site Cl atoms to Au-Au mid-position. We calculated band gap by reflecting these changes independently. Then, we synthesized $Cs_2Ag^IAu^{III}Cl_6$, $Cs_2Cu^IAu^{III}Cl_6$ and estimated band gap by taup plot of diffuse reflectance spectra.

[Results and discussion] The band gap of $Cs_2Au^IAu^{III}Cl_6$ in ambient pressure condition was 1.21 eV. We could evaluate the effect of structural change on bad gap as follows:

(1): contraction of *a,b*-axes made band gap increased (0.74 eV / Å :amount of change).

(2): contraction of *c*-axis made band gap decreased (0.17 eV / Å).

(3): moving to Au-Au mid-position of 8*h* site Cl atoms made band gap decreased (6.2 eV / Å).

(4): moving to Au-Au mid-position of 4*e* site Cl atoms made band gap decreased (2.4 eV / Å : place close to mid-position, 0.44 eV / Å : place far to mid-position).

There are three different crystal structures (T, C, U) in $Cs_2Ag^IAu^{III}Cl_6$ and, two different crystal structures (U,U') in $Cs_2Cu^IAu^{III}Cl_6$. In these compounds, band gap values were estimated as $Cs_2Au^IAu^{III}Cl_6$: 1.18 eV, $Cs_2Ag^IAu^{III}Cl_6$: 1.32 eV (T), 1.39 eV (U), 0.84 eV (C), $Cs_2Cu^IAu^{III}Cl_6$: 0.64 eV (U), 1.14 eV (U'). These results show adjastability of band gap between 0.64 eV - 1.39 eV through 8*h* site Cl position. In other respect, the position of 8*h* site Cl which couldn't be determined precisely by Rietveld analysis of powder XRD pattern, can be estimated by matching calculated band gap from Wien2k with the value from diffuse reflectance measurement.